

Crossbonding of Casein Bristle Fiber *

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Abstract

A method is described for reducing the rate of water uptake of casein fibers and plastics. The method involves treating formaldehyde-hardened casein products with resorcinol and formaldehyde, drying, and heating. Optimum conditions for this treatment are described. The results indicate that resorcinol forms crossbonds with casein and formaldehyde.

Introduction

Casein bristle fibers were developed at this laboratory by McMeekin and associates. The process is a simple one, involving only the addition of water to acid-precipitated casein, extruding it through a die heated to 100°C, passing the fibers through a for-

maldehyde solution, and drying [9]. This process has been utilized commercially to produce casein fiber. The equipment used has been described by Bendigo [1]. Casein bristles are potentially useful in brushes and in the coiled form in upholstery filling, mattresses, and air filters. Casein bristles have satisfactory solvent resistance in oil-base paints, but are softened by the new rubber emulsion paints, which have a water base.

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The patent literature contains numerous claims for the improvement of wool and artificial fibers produced from protein by impregnation with hydrophobic synthetic resins. Since our work was first reported [11], Johnson described the reaction of phenols and formaldehyde with wool [7]. Windus reported data on the acid-catalyzed reaction of resorcinol and formaldehyde with hide substance [16, 17]. The basic reactions involved were described by Fraenkel-Conrat and Olcott in 1948 in a study of the crosslinking of proteins by formaldehyde [5]. In a typical Mannich reaction [2], the ϵ -amino groups of lysine form a methylol, which reacts with the phenol. Our original purpose in investigating these reactions was to determine whether the formaldehyde that had reacted to the methylol stage but had not formed crossbonds [13] would form those bonds if a small amount of an intermediary compound were added. The present paper describes a resin treatment in which substantial amounts of phenols and formaldehyde are bound to the protein fiber and some additional crossbonds are formed.

Experimental

Casein bristle fiber was produced for this study by continuous production from a screw extruder. The $1\frac{1}{8}$ -in. diameter screw was driven by a 2-HP motor at 30 r.p.m. The die was $\frac{1}{4}$ -in. thick and contained 10 holes, 0.010-in. diameter, at the delivery end. To reduce the back pressure, however, the holes had a 30° countersink extending within 0.010 in. of the delivery end. The casein mixture was 40% water and 60% high-quality acid-precipitated casein. The threads issued at 300 ft./min. and were drawn off by a rotating drum 10 ft. in circumference. The hot threads from the die fell into a 3% bentonite suspension containing 5% formaldehyde, passed under a roller to change their direction, and then were wound on the wheel. The hardening took place over 24 hrs., while the bristle was drying out on the drum. The finished fiber contained about 3% formaldehyde and had a dry strength of about 0.7 g./den., a wet tenacity of 0.2 g./den., and a denier ranging from 600 to 1200, depending on extrusion conditions.

For the measurement of reagent absorption, the dried bristle was conditioned at 73°F and 50% R.H. for several days and then cut into 9-cm. lengths. Groups of 10 fibers were weighed, placed in a test tube and then used for the various experiments. Following the reaction, the fibers were centrifuged in

a basket centrifuge to remove the excess reagent, dried on wire gauze at room temperature, and then heated, usually for 1 hr. at 110°C. From the weight uptake of the fiber, compared with a control which was given only the heat treatment, the amount of reagent absorbed was calculated on the basis of the dry weight.

Tensile strength measurements were made on a Scott IP-2 Serigraph. A 2-in. gage length was used for the wet and dry tests. Fibers measured wet had been soaked for 4 hrs. in distilled water unless otherwise stated. The treated fibers were weighed individually on a microtorsion balance, placed in separate tubes of water, and broken within a few seconds after removal from the water. Chart paper was used to face the clamps of the machine. Knot tests were made with a single overhand knot in the fiber. In order to attain equilibrium quickly, fibers that had been resin-treated and baked were soaked for an hour in distilled water, centrifuged and dried, then equilibrated for 16 hrs. before being tested for knot strength. All figures are the average of 10 individual breaks.

Results and Discussion

Table I shows the results obtained when casein bristle fibers, hardened with formaldehyde, were immersed in a test tube containing an aqueous 0.01M

TABLE I. EFFECT OF ABSORBED PHENOLS ON THE WET TENACITY OF TREATED CASEIN BRISTLE (0.01M SOLUTIONS, 16 HRS. AT 25°C)

Phenol	Uptake, % of substance	Wet tenacity, g./den. after $\frac{1}{2}$ hr.
Control	—	0.18
Phenol	6.6	0.17
Metacresol	16.8	0.21
Hydroquinone	7.2	0.17
Catechol	9.0	0.23
Resorcinol	8.4	0.20
4-chlororesorcinol	16.1	0.40
4-carboxyresorcinol	26.6	0.38
Pyrogallol	8.2	0.19
Phloroglucinol	9.3	0.26
4-sulfo-resorcinol	11.4	0.21
2,2' 4-4'tetrahydroxydiphenyl sulfide	7.3	0.33
4-4'dihydroxy diphenyl sulfone (20% EtOH)	15.8	0.21
4-4'dihydroxy diphenyl sulfide (15% EtOH)	20.4	0.61
α -naphthol (20% EtOH)	17.2	0.55
β -naphthol (20% EtOH)	16.9	0.26
2,4,2'5'tetrahydroxydiphenyl	12.6	0.21

solution of a phenol for 16 hrs. at 23°–25°C. Phenols that were not water-soluble to this extent were dissolved with the aid of 5%–20% ethanol. The fibers were centrifuged and dried at 110°C and the wet tenacity was determined after they were soaked in distilled water for $\frac{1}{2}$ hr. The weight uptake is given on the basis of the oven-dry fiber.

Since the phenol is no longer soluble in water or organic solvents after the baking step, it apparently has reacted with the formaldehyde in the fiber. There seems to be a specific relation between structure and the power to increase the wet strength of the fibers. Metacresol was absorbed in as large amounts as 4-chlororesorcinol and 4-carboxyresorcinol but did not raise the wet strength. 4,4'-Dihydroxydiphenyl sulfide and α -naphthol gave good wet strengths, but they have to be applied from alcoholic solution. The sulfone corresponding to the sulfide was absorbed in large amounts but did not increase the wet strength. Although resorcinol itself did not increase the wet strength, three of the compounds that did are resorcinol derivatives. For this reason, the simpler resorcinol was investigated more extensively.

Further evidence of the mechanism of the reaction was sought by studying the stress-strain curve of the resorcinol-treated fiber after it had been soaked for 4 hrs. in distilled water. It showed considerably increased breaking elongation, but no improvement in wet strength. If the added resorcinol is attached to the protein by means of the methylol groups, it is possible that after-treatment with formaldehyde might still further crossbond the protein fiber. To test this idea, fibers were treated in 2% resorcinol solutions for 16 hrs. at room temperature, and without drying were then placed in various concentrations of formaldehyde. After drying at room temperature and heating at 110°C for 1 hr., the fibers were tested. Figure 1 shows the results. The reduction in flow and increase in yield point for the wet fiber clearly indicate that additional crossbonds have been formed. The wet strength calculated from these curves shows that the wet tenacity increased from 0.2 to 0.38 g./den.

A further simplification of this process was possible if the relative reactivities of the phenol and formaldehyde with each other were low, compared with the rate of reaction with the protein. In the absence of added acid or basic catalyst, a solution containing formaldehyde and 1% resorcinol did not precipitate polymer for 2 weeks at room temperature, if the ratio of formaldehyde to resorcinol was 8 to 1 or lower.

Since the reactions of formaldehyde and phenol are catalyzed by acid or base, it appeared likely that an optimum pH might exist for the reaction with casein fiber. Consequently, the effect of pH was investigated. Dilute HCl and NaOH were used to shift the pH of a 1% resorcinol-1.1% formaldehyde solution. With USP formaldehyde and reagent grade resorcinol, the pH value is normally 3.6. After treatment for 16 hrs. at 23°–25°C, the fibers were dried and then heated at 110°C for 1 hr. The results in Table II, indicate that the wet strength of the fiber is optimum over a fairly large pH range. On the acid side the working life of the solutions was greatly decreased and on the alkaline side a deep-brown color due to oxygen absorption was apparent. Since the reaction at pH 3.6 produced a minimum of side reactions between the resin components [15] and did not interfere with the absorption of resin by the fiber, this pH value was used in the remainder of the work. Trial mixtures of formaldehyde and

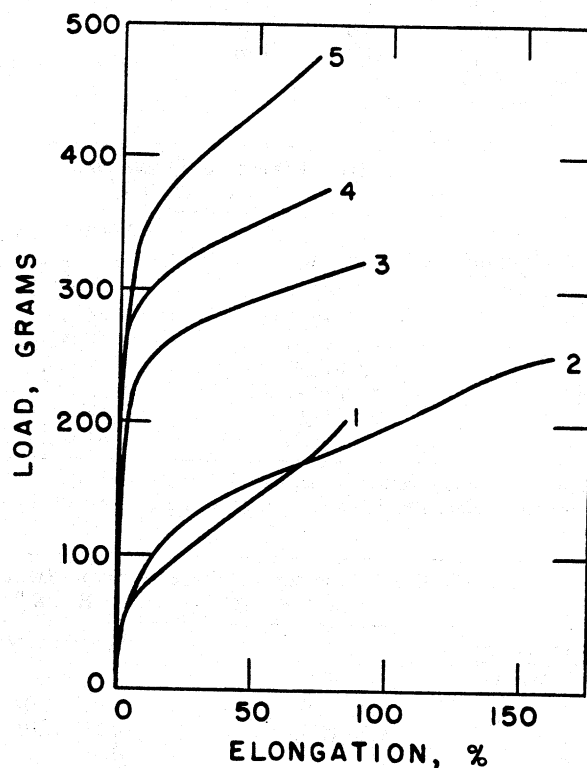


FIG. 1. Effect of treatment with resorcinol or resorcinol followed by formaldehyde. (1) control bristle; (2) bristle treated for 16 hrs. in 2% resorcinol; (3) same as (2) after treatment for 1 hr. in 5% CH_2O ; (4) same as (2) after treatment for 4 hrs. in 5% CH_2O ; (5) same as (2) after treatment for 24 hrs. in 5% CH_2O .

phenol, metacresol, catechol and hydroquinone, under more acid conditions, did not give the high wet strengths obtained with resorcinol. Paracresol dimethylol and the trimethylol of phenol were also ineffective in increasing wet strength.

The effect of the formaldehyde-resorcinol ratio in the solutions on fiber properties was determined. In addition, the fibers were treated for varying lengths of time, dried at room temperature, and baked at

110°C. Table III shows the regular increase of wet strength and resin content with length of treatment.

At 1:1 ratio, no increase in wet strength accompanied the absorption of resin. A regular increase in resin content with length of treatment was apparent. The higher formaldehyde-resorcinol ratios increased the rate of absorption. High concentrations of formaldehyde alone did not produce any effect.

Precondensation of resorcinol and formaldehyde has been claimed to be of advantage in improving the resistance of wool and casein fiber [8] to water and hot acid dyebaths. When our continuous filament casein fiber [12] was treated with such a resin, the color of the fiber changed slightly to an off-white. In attempting to dye the fiber, contact with the hot acid dyebath changed the color to deep orange-brown. This would certainly be an obstacle to dyeing any color except brown or black. When casein bristle was treated with such a resin, the color of the bristle after heating was tan or brown, the same as with the uncondensed resin. The initial absorption of resin proceeded at a higher rate than that for the uncon-

TABLE II. EFFECT OF PH OF RESORCINOL-FORMALDEHYDE SOLUTIONS ON WET STRENGTH OF CASEIN BRISTLE

pH	Wet tenacity, g./den. at 4 hrs.	Resin uptake (%)	Aging of solution at 16 hr.
1.6	0.22	9.7	Pink precipitate
2.0	0.20	12.3	White precipitate
2.3	0.20	14.7	Hazy
2.8	0.26	13.5	Clear
3.6	0.29	14.0	Clear
5.2	0.28	13.6	Clear
5.6	0.28	13.8	Tan
6.6	0.11	11.2	Brown
Control fiber	0.18	—	—

TABLE III. EFFECT OF FORMALDEHYDE-RESORCINOL RATIO ON WET STRENGTH AND RESIN UPTAKE OF CASEIN BRISTLE*

Ratio	formaldehyde† resorcinol	Wet tenacity, g./den. after 4 hrs. in H ₂ O			
		1 hr. in resin	22 hrs. in resin	52 hrs. in resin	160 hrs. in resin
	1:1	0.22 (2.1)	0.25 (7.4)	0.26 (9.8)	0.23 (11.9)
	3:1	0.29 (1.7)	0.29 (8.8)	0.30 (10.2)	0.42 (13.4)
	6:1	0.28 (2.6)	0.33 (9.0)	0.40 (10.9)	0.57 (14.6)
	12:1	0.30 (2.8)	0.41 (9.5)	0.44 (13.6)	0.69 (15.9)
	18:1	0.30 (3.0)	0.49 (10.3)		
	24:1	0.30 (1.8)	0.53 (11.0)		

* Resin uptake is given in parentheses after wet strength.

† Resorcinol concentration kept constant at 1%; formaldehyde was varied.

TABLE IV. EFFECT OF FORMALDEHYDE-RESORCINOL RATIO OF PRECONDENSED RESINS* ON WET STRENGTH AND RESIN UPTAKE† OF CASEIN BRISTLE

Ratio	formaldehyde resorcinol	Wet tenacity after 4 hrs. soaking g./den.			
		1 hr.	22 hrs.	54 hrs.	144 hrs.
	1:1	0.22 (6.0)	0.24 (11.0)	0.25 (11.5)	0.29 (15.5)
	2:1	0.23 (7.5)	0.27 (12.0)	0.31 (17.0)	0.42
	4:1	0.24	0.31	0.34	—
	6:1	0.28 (10.0)	0.36 (13.5)	0.40 (15.5)	0.61 (16.0)
	12:1	0.28 (2.0)	0.46 (10.1)	0.55 (13.1)	—
	18:1	0.27 (1.7)	0.43 (8.4)	—	—
	24:1	0.28 (1.5)	0.54 (9.9)	—	—

* Precondensed resin was made by heating the resorcinol and the formalin solution, 39.5% wt./v., together for $\frac{1}{2}$ hr. at 60°C and then diluting to 1% resorcinol concentration [8]. Dr. Halwer of this laboratory estimated by light-scattering measurements that an 8.8:1 resin had an average molecular weight of 400 ± 100 after $\frac{1}{2}$ hr. of condensation.

† Resin uptake is given in parentheses after fiber tenacity.

densified components. As shown in Table IV, however, the wet tenacities were usually within the standard deviation, 0.03 g./den., of the corresponding value in Table III, when the precondensation step was omitted.

As the ratio of formaldehyde to resorcinol increased, the absorption of the resin passed through a maximum and then decreased. This was not true of the uncondensed series and probably indicates that the higher molecular weight of the resin was cutting down the rate of penetration into the fiber. The precipitability of the resin by dilution with water is also a measure of its size. When USP Formalin, 30 ml., and resorcinol, 5 g., were heated together at 60°C, (molar ratio 8.8 to 1), after 4½ hrs. heating the resin clouded when 50 ml. of water was added. After 6½ hrs. heating, 1 ml. of the resin clouded with 5 ml. of water and precipitated with 6 ml. Precondensed resins were not studied further, since the wet strengths were no better than those shown in Table III and because of the much shorter working life of the solutions.

The effect of the resin on dry tenacity and flexibility must be considered when treated bristle is to

be used in brushes. With a low formaldehyde-resorcinol ratio some of the bristles were brittle when the resin content exceeded 10%. High concentration of the resin in the treating solution had the same effect. Fibers were treated for 1 hr. with solutions containing high ratios of formaldehyde to resorcinol, and then dried and baked at 110°C for 1 hr. Table V shows the decrease in flexibility with increase in resorcinol concentration.

In this series the best water resistance and flexibility were obtained at 1% resorcinol concentration. Lower concentrations showed no improvement. Another factor in the brittleness of the fiber is overheating during the baking process. A series of bristle fibers was treated in a 5% resorcinol solution with 6 to 1 formaldehyde-resorcinol ratio for 16 hrs. at room temperature and then dried at room temperature. The effect on flexibility when the fibers were baked at various temperatures is shown in Table VI.

Little improvement in wet strength resulted until the fibers were heated above 65°C. Because of the high resin content, however, the flexibility was impaired even when the fibers were dried at room temperature. In a water-resistant surface coating for protein plastics this lack of flexibility would be of less consequence than in fibers.

TABLE V. EFFECT OF RESORCINOL CONCENTRATION ON FLEXIBILITY OF CASEIN FIBER

Resorcinol concentration in solution (%)	Ratio formaldehyde:resorcinol	Dry tenacity (g./den.)	Flexibility† (%)	Wet 4 hrs., tenacity (g./den.)
1.0	24:1	0.57	100	0.43 (4.2)*
2.0	24:1	0.75	93	0.37 (7.6)
3.0	24:1	0.76	90	0.33 (8.6)
5.0	24:1	0.74	88	0.30 (7.1)
7.5	12:1	0.78	80	0.34 (11.4)

* Resin absorbed.

† Ratio $\frac{\text{tenacity knotted fiber}}{\text{dry tenacity}}$.

TABLE VI. EFFECT OF HEATING ON PROPERTIES OF CASEIN BRISTLE

Tem. perature (°C)	Dry tenacity	Flexibility (%)	Wet tenacity (g./den.)	Resin (%)
25	0.61	68	0.22	24.4
35	0.69	56	0.21	23.2
45	0.75	—	0.21	23.3
55	0.67	42	0.23	27.9
65	0.60	39	0.25	26.6
75	0.74	—	0.40	24.6
85	0.83	—	0.73	26.0
95	0.85	—	0.68	25.5

TABLE VII. EFFECT OF RESIN TREATMENT ON PROTEIN DISCS HARDENED WITH FORMALDEHYDE

Protein	Treating solution		Resin uptake (%)	Water absorption at 24 hrs. (%)	Water absorption at equilibrium (%)	Days to reach equilibrium
	Resorcinol (%)	CH ₂ O (%)				
Casein	0	0	0	33.0	34	3
Casein	5.0	6.4	11.0	2.5	22.6	11
Casein	14.3	32.5	11.6	2.2	23.2	16
Casein	25.0	29.0	13.3	1.4	21.9	23
Soybean	0	0	0	19.0	19.8	2
Soybean	25.0	29.0	11.4	1.25	19.4	20
Zein	0	0	0	12.7	15.5	5
Zein	5.0	5.5	14.5	4.7	15.8	8

TABLE VIII. EQUILIBRIUM SWELLING OF RESIN-TREATED CASEIN BRISTLES

Resin content (%)	Moisture at equilibrium (%)	Swelling ratio*
0	33.2	1.64
5.2	30.4	1.58
8.7	27.6	1.51
16.2	23.5	1.41
23.4	20.0	1.33
25.2	18.0	1.29
28.5	20.4	1.34

* Ratio $\frac{\text{swollen volume}}{\text{original volume}}$.

Two-inch diameter discs were molded from powdered casein, soybean protein, and zein that had been previously hardened with formaldehyde and contained about 10% water [6]. The discs were placed in resorcinol-formaldehyde solutions (Table VII) for 16 hrs. at room temperature and then dried at room temperature and baked at 100°C for 2 hrs. The effect on water absorption of the discs, which were only $\frac{1}{8}$ in. thick and reached equilibrium rapidly [10], was considerable.

The treatment discolored the discs, but the addition of sodium bisulfite to the treating solutions will decrease the amount of brown color generated during the heating process. Cross sections of the discs showed that the brown color was in the outer part of the discs. Measurements for density were made in organic liquids by N. J. Hipp, of our laboratory, on samples taken by milling the discs to different depths. They showed that the the outer layers were more dense, 1.324–1.333, and probably contained more of the treating resin than the average composition indicated. The inner part of the discs had a density of about 1.283. Resin prepared by evaporation and baking of an 8:1 resin had a density of 1.386.

Since we had observed that the wet strength of casein bristles is lowered by increasing the soaking times to more than 4 hrs., a test was applied to see whether actual additional crossbonds were formed or whether there was merely dilution with a nonabsorbing resin which decreased the rate of water uptake.

A series of casein fibers was treated with a solution containing 5% resorcinol and a 6/1 ratio of formaldehyde for various lengths of time. The bristles contained from 4% to 28.5% resin. When these fibers were allowed to stand in water for 3 days

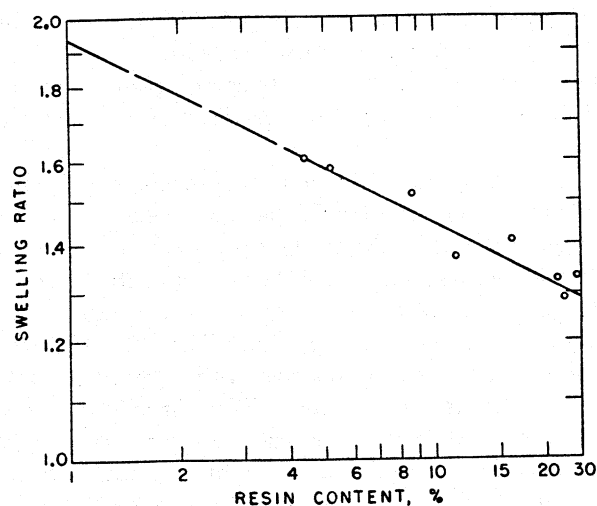


FIG. 2. Test for crossbonding. Log/log graph of swelling ratio against resin content of casein bristle fiber.

the maximum swelling was reached. By rapidly wiping the fiber, weighing it at 15-sec. intervals and extrapolating to zero time, a series of values was obtained for equilibrium water uptake. At 48 hrs. the water uptake reached the values given in Table VIII.

Preston and Nimkar [14] used the log of the swelling ratio plotted against log of the resin content as a test for crossbonding. This is based on the Flory-Rehner theoretical equation for equilibrium swelling of a crosslinked polymer [4]. For this purpose the equation can be reduced to $-V_0 = \text{constant} \times M_c^{3/5}$, where V_0 is the swelling ratio (swollen volume/original volume) and M_c is the weight of the polymer chain between crosslinks. For slightly crosslinked styrene-divinyl benzene gels, it has been shown by Boyer and Spencer [3] that $M_c = k c^{-a}$, where c is the concentration of the crosslinking agent. As shown in Figure 2, the slope of the plot is $-.074$, so a is $-.1235$, and thus the new crosslinkages introduced are proportional to the eighth root of the resin concentration.

When data relating wet strength to resin content were plotted, it was found that increases in the formaldehyde-resorcinol ratio up to 12 to 1 produced higher wet strengths for the same amount of resin, but that increases above this amount produced no further improvement. Other phenols produced more efficient resins, notably 4-4'-dihydroxy-diphenyl sulfide. Phloroglucinol reacts too rapidly with formaldehyde for use in a mixed solution. Treatment of

TABLE IX. RELATIVE STIFFNESS OF CASEIN BRISTLES

	Modulus of stiffness* (in./lbs.)	
	Wet	Dry
Casein, formaldehyde-hardened	1.04×10^4	10×10^4
Casein, resin-treated	$3-4 \times 10^4$	14×10^4
Hog bristle	7×10^4	40×10^4

* When bristles are soaked in water for short periods, values for stiffness will be higher than the figures given here.

a formaldehyde-hardened bristle with phloroglucinol, alone, and then with formaldehyde resulted in absorption of a substantial amount of resin.

Substitution of other aldehydes for formaldehyde produced no improvement. Glyoxal, malonaldehyde, and succinaldehyde were used with resorcinol. Succinaldehyde produced about equal wet strengths; glyoxal and malonaldehyde were inferior. Acetone and furfural did not raise the wet strength.

A quality of bristles directly related to their performance in brushes can be evaluated by measuring the stiffness of wet single bristles on the Olsen-Tour-Marshall stiffness tester. Although the wet stiffness of the bristle was low, the modulus could be computed at equilibrium swelling by using a span of only $\frac{1}{8}$ in. and the lowest range, .05 in.-lb. Table IX shows the results.

Conclusions

The optimum conditions for reaction of resorcinol and formaldehyde with casein bristle fiber hardened with formaldehyde are: (1) high formaldehyde/resorcinol ratio, 12/1 or higher; (2) absorption at room temperature; (3) pH of 3.6; (4) baking temperature of 75°–110°C. With these conditions, the wet strength of treated fibers is raised considerably up to 4 hrs. of soaking in water. If the soaking is prolonged, the resin treatment considerably increases the time required to reach equilibrium. The ultimate wet strength is increased by 50% over the control, however, regardless of the time of soaking.*

* Mention of any specific equipment or products in this paper does not imply that these products are endorsed or recommended by the U. S. Department of Agriculture over others not mentioned.

Acknowledgment

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